PHYSICAL CHARACTERIZATION ON HYDROTHERMAL CARBONIZATION AND TORREFACTION PRODUCT FROM WOOD FIBER WASTE

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ABSTRACT

The world today is faced with serious global warming and environmental pollution. Besides that, the fossil fuel will become decrease in the near future and also increasing prices of fuel cause awareness to find alternative energy. Carbon is one of the most abundant elements found on earth. Nowadays carbon is really useful in the chemical industries and the demand of carbon used is high based on its applications towards the human needed. Carbonization is one of the possible thermo chemical conversions of biomass into energy, where a solid residue known as charcoal is produced through a slow process of partial thermal decomposition of in the absence or controlled presence of oxygen. (Bridgewater, 2003). There are three objectives that need to achieve at the end of this research. The objectives are; to develop and demonstrate the technology of hydrothermal carbonization process; to compare the carbon particles produce from HTC process and pyrolysis process; to study the effect of the wood fibre waste used towards the production of carbon. The HTC process occurs in the excess of water. About1 liter water was used for every experiment of hydrothermal carbonization process. The reaction is based on catalyst which is 50ml of citric acid was used for every experiment of hydrothermal carbonization process.the reaction occur in the supercritical unit for temperature about 200^{o}C. The product obtained then was drying to remove the water contain. Second process which is the pyrolysis was run in the furnace by using the same operation condition as the HTC process. The differences between the process is the pyrolysis is no including water during the process. The process is about heating the wood fiber waste with absence of oxygen. Then the products were undergoing the physical characteristic testing by using Field Emission Scanning Electron Microscopy (SEM) and Nuclear Magnetic Resonance (NMR). After analyzing the sample from both process through FESEM and NM) the comparison was made. Through the FESEM characterization, the diameter of the sample and the

morphology effect was determined. The comparison was made and the best sample shown by the sample from HTC process using 150g of wood fiber waste. The diameter of the sample shown about 7.3μm and the highest rupture occur at the surface of the particles. Results from NMR proves that the carbon content inside the sample was changes after undergo the HTC and pyrolysis process. The comparison was made and it shows that after undergo the HTC process the carbon content for cellulose and lignin was increased and HTC sample shows the content of aromatic lignin. Differ with pyrolysis process which does not contain aromatic lignin but for other content still increase after undergo the pyrolysis process. The proximate analysis also was done and it was found that HTC 175g WF gives the highest value of moisture content, HTC 150g WF gives the highest values of ash content with15.07%. for volatile content the highest values was the sample from pyrolysis 175g WF with 91.89% and lastly for calorific value proves the pyrolysis with 175g of WF give the highest calorific value with 24.88 MJ/kg.

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LIST OF SYMBOLS

μm	Micrometres
M	Molar
Mg	Milligram
g	Gram
hr	Hour
L	Litre
m	Meter
cm	Centimetre
%	Percentage
MW	Molecular Weight

LIST OF ABREVIATIONS

HTC	Hydrothermal Carbonization
TF	Torrefaction
FESEM	Field Emission Scanning Electron Microscopy
NMR	Nuclear Magnetic Resonance

CHAPTER 1

INTRODUCTION

1.1 Research Background

Carbon is one of the most abundant elements found on earth. Nowadays carbon is really useful in the chemical industries and the demand of carbon uses is high based on its applications towards the human needed. Naturally carbon was founded from earth which is residue from the petroleum refinery also called as coal or charcoal. As limited number of petroleum founded from days to days, other alternative was found in order to produce carbon particle continuously. One of the best alternatives is by converting the biomass into the carbonaceous materials. Biomass is defined as the biological material derived from living or recently living organisms. In the other words, biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, nitrogen and also small quantities of other atoms like alkali, alkali earth and heavy metal.

Biomass can be divided into several types which are wood and agricultural products, solid waste, landfill gas and biogas and alcohol fuels. The main focus of this research is on the wood waste. Wood waste like logs, chips, bark and sawdust accounts for about 46 percent of biomass energy. A large proportion of wood fiber wastes produce by the agricultural activities and forest today become global issues in managing the waste to be reused or recycled compared just thrown away to the landfill. Knowing the carbon used to construct biomass is absorbed from the atmosphere as carbon dioxide (CO_2) by plant life using energy from the sun. If the plant is broken down or die it will release the carbon back to the atmosphere mainly as either carbon dioxide (CO_2) or methane (CH_4) depending on the conditions and processes involved. As the wood fiber waste is thrown away to the landfill it will contribute towards the releasing back the carbon dioxide to the atmosphere. Besides that it by thrown away to the landfill it will reduce the space of earth. The proper way in managing, reusing and recycling the wood fiber waste is important in order to reduce the wood fiber waste in landfill.

Direct combustion is the old method in converting biomass into energy but only in about 10 percent of energy produce. The conventional method was not environmental friendly process since during the combustion the present of oxygen during process will cause the large amount of carbon dioxide release to the atmosphere. Usually the common way in converting the biomass into the value added product is by using pyrolysis process. The process of pyrolysis is about heating the biomass in specific temperature in absence of oxygen. The absence of oxygen during the process will help to reduce the carbon dioxide release to the atmosphere beside maintain the quality of the carbon produce. Pyrolysis can be divided into two types which is slow pyrolysis and fast

pyrolysis. The key words that represented the pyrolysis process are temperature. Slow pyrolysis will occur if the reaction temperature less than 450^{o}C while the fast pyrolysis will occur when the temperature applied greater than 800^{o}C. New alternative was founded in converting the biomass to the carbon which called as hydrothermal carbonization process (HTC).

Hydrothermal carbonization process will convert biomass into the valuable product which is carbon particle based on thermal processes. Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material. Actually biomass can equally apply to both animal and vegetable derived material. Besides that, biomass is carbon based and is composed of a mixture organic molecules containing hydrogen and usually including atoms of oxygen, often nitrogen and also small quantities of other atoms like alkali, alkaline earth and heavy metals. These metals are often found in functional molecules such as the porphyrins which include chlorophyll that contains magnesium.

Dehydration is the main chemical reaction in the hydrothermal carbonization process. This is due to the high carbon content in the final product. In the other words, hydrothermal carbonization is an exothermal process that lowering both the oxygen and hydrogen content of the feed using mainly dehydration. Carbonization is one of the possible thermo chemical conversions of biomass into energy, where a solid residue known as charcoal is produced through a slow process of partial thermal decomposition of in the absence or controlled presence of oxygen. (Bridgewater, 2003). There are a few parameters that need to be considering during the process take place which are

temperature and pressure, time of reaction, volume of water and concentration of catalyst. All of the parameters will strongly affect the carbon produce at the end of the process. The comparison can be made and the best carbon produce can be choosing easily through the series of testing with different parameters applied.

Characterization is also important in analyzing the result obtained. The properties of the carbon produce can be obtained fro the characterization for example the chemical and physical characteristic of the carbon produce. The chemical characteristic is about the composition of the carbon produce and the physical characteristic is about the shape, color, the diameter of the carbon produce and others. Besides that, the comparison between the carbon produce from the pyrolysis and hydrothermal carbonization process can be done. The characteristic involve in analyze the morphology of the product. Morphology defined as the study of the physical characteristic of the sample in terms of surface area, shape of molecule, molecule content, diameter of the particle and others. Further study on the process will cover in chapter 2.

1.2 Problem Statement

Nowadays, a large proportion of the woody waste generated which consists of used particleboard, sawdust and others from the industrial activities becoming the global issue in terms of managing the wood fiber waste to be recycled compare to thrown-away to the landfill. Edward Madigan (2012) state that since the turn of this century, world has been dubbed by some "the throw-away society", and it generates 50 percent of the world's solid and industrial waste. "The throw-away society" is the society that just simply thrown away the rubbish to the landfill. Almost half the municipal solid waste that goes into landfills consists of paper and wood fiber.

Based on the above facts, concern about the global warming and environmentally friendly processes for converting the wood fiber waste to the value added product is raised. Also the need for research that aims to develop clean technology or in the other words new process that reduces waste and pollutants is mentioned. From this problem, the new and environmentally sustainable process of carbon was developed through aqueous media. This process called as the hydrothermal carbonization process (HTC). Hydrothermal carbonization process is the process that converting biomass into value added product with less environment pollution effect due to no carbon dioxide release during the process. The process is about to lower the oxygen and hydrogen content of the feed using mainly dehydration process. The process is exothermic process which occurs at high temperature in range $180^{o}C$ – $300^{o}C$ and under pressure.

1.3 Research Objectives

There are three objectives that need to be achieving at the end of this research. The objectives are:

1. To develop and demonstrate the technology of hydrothermal carbonization process.
2. To make a comparison of carbon produce from the hydrothermal carbonization process and pyrolysis process.
3. To study the effect weight of biomass used on morphology characteristic.

Hydrothermal carbonization is the method in producing carbon particles with wood fiber waste as the raw material.This process is one of the alternatives on converting the biomass into the value added product. The process of hydrothermal carbonization occur subcritical condition in which at high temperature and pressure. The detail of the hydrothermal carbonization process will be discussed in section 2. Since the old method of converting the biomass is pyrolysis process, the comparison of the carbon produce from the HTC process and the pyrolysis was made. The comparison was made in terms of physical characteristics. The characteristic of the product will be investigated through Field Emission Scanning Electron Microscopy (FESEM) and Nuclear Magnetic Resonance (NMR) and the result obtained from the characterization will be used to make the comparison. The further characterization process will be discussed on chapter 3.

1.4 Significance of Proposed Study

The study is about the production of the carbon from the process of hydrothermal carbonization process by using wood fiber waste as the biomass. Hydrothermal carbonization process is the most environmental friendly process as the carbon dioxide (CO_2) release through the process is less compare to the combustion. This is because the process is dehydration process which is only oxygen and hydrogen will release as the carbon need to be in solid form. Besides that this process will reduce the waste of wood by converting the waste to value added product which is carbon. As the result, the wood fiber waste generated will be recycled and it will reduce the waste and pollution to the landfill.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The main resource for the literature search was the research journal with title "The Production of Carbon Materials by Hydrothermal Carbonization of Cellulose". This source was really fulfilled with the title of the research which is "Morphology Studies on Hydrothermal Carbonization Product from Wood Fiber Waste". Combinations of the following keywords were used to identify relevant material; carbon particles, wood fiber waste, hydrothermal carbonization process and others.

A limited number of studies were found that carbon particles give many applications in the chemical industries. Kim (2011) states in his article titled "Electrochemical Uses of Carbon" that the carbon is the one of the most abundant elements found on earth. According to Titirici et al (2009), carbon particles are

synthesized under hydrothermal conditions using different biomass (glucose, xylose) and biomass derivatives (s-hydroxymethyl-furfural-1-aldehyde and furfural) as a carbon sources. The emergent themes may be divided into five broad areas; history and background of carbon particles; properties of carbon particles; application of carbon particles; wood fiber waste; and hydrothermal carbonization process.

2.2 Wood Fiber Waste as Biomass

According to Jay (2012), biomass is defined as any organic material that comes from plants or animals. The others research from Libra et al (2011) stated that biomass has been assigned many roles to play in strategies for sustainable consumption. In addition, other than being a food source and renewable raw material, it can be used for energy production, carbon sequestration and finally, as an essential element to increase soil fertility. Biomass energy resources are plentiful. Anything that will decompose and burn can be used as biomass energy. Grass clippings, animal waste, corn stalks, acorns, tree limbs, meal scraps and others can all be used for biomass energy. The utilization of woody biomass for a variety of products, including energy, has increase in recent years. Based on DeAnna (2011), due to the growing interest in climate change, the environment, and energy security, woody biomass is receiving more attention as a renewable energy source. Woody biomass has become the topic of intense regarding its sustainability, cost effectiveness and greenhouse gas impact.

Recycling today constitutes that most environmentally friendly method of managing wood waste. A large proportion of the wood generated consists of used furniture and other constructed wooden items, which are composed mainly of particleboard, a material which can be potentially be reused. (Charalampos et al, 2007). Similarly, the other research from Todd et al (2007), woody biomass holds a great potential as a renewable source for bio-based materials, feed stock and energy. Besides that the use of renewable energy has been widely discussed as an alternative to fossil fuels. The biomass, consisting mainly of agricultural and forestry waste can be regarded as a renewable energy source with potential to supply the global energy demands. Moreover the use of biomass contributes to reduce the greenhouse effect. (Marcela et al, 2011). The information gain from U.S Energy Information website (2008), biomass energy is derived from three distinct energy sources: wood, waste, and alcohol fuels. Wood energy is derived both from direct use of harvested wood as a fuel and from wood waste streams. The largest source of energy from wood is pulping liquor or "black liquor," a waste product from processes of the pulp, paper and paperboard industry.

Besides that Robert (1993) state that we are facing a serious challenge in the United States in dealing with municipal waste landfills that are near or at capacity. Wood waste including wastepaper, construction waste, demolition waste, and tree trimmings make up a significant portion of this municipal waste.

2.3 Effect of Wood Fiber Waste on Environment

As the demand for biomass has grown, so has the number of criticisms and misconceptions about it. One of the major effects of biomass towards the environment is that the burning of biomass as fuels releases carbon dioxide (CO_2) and other greenhouse gases which are contributing to global warming. In reality, woody biomass is a carbon neutral energy source. According to DeAnna (2011), trees are part of an atmospheric cycle. As they grow, they absorb carbon from the atmosphere temporarily storing it. When a tree dies, the same amount of carbon that it absorbed during its lifetime is released back into the atmosphere as it decomposes, adding no new carbon to the atmosphere. When woody biomass is burned to produce to produce energy, it released that same amount of carbon that would have naturally been released if the tree had been left to decompose on the forest floor.

Other research from Roger *et al* (2010), wood material is composed of about 50% carbon by dry weight, this carbon having been drawn from the CO_2 removed from the atmosphere by the growing tree. In other words, wood products provide a physical storage of carbon that was previously in the atmosphere as a greenhouse.

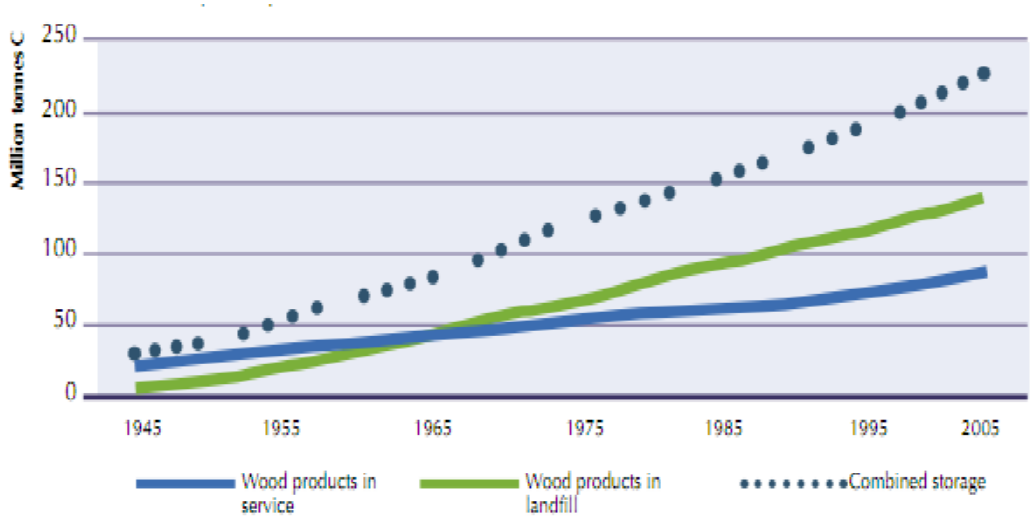

Figure 2.1 Net carbon storage in wood and paper product and landfills in Australia. (Source: Australian Greenhouse Office Wood Products Model)

The figure 2.1 shows that the carbon storage in the wood product and landfills in Australia is increase every year. It proves that the wood fiber is the best carbon removal from the atmosphere which is contributing in decreasing the effect of greenhouse. However, burning biomass for energy provision increase the amount of carbon in the air just like burning coal, oil or gas if harvesting the biomass decreases the amount of carbon stored in plants and soils or reduces carbon sequestration.(Helmut et la, 2012). Based on Aaron (2012), the rate at which trees release that CO_2 depends on how they are managed by human. If the tree is allowed to die and rot, its carbon is released into the soil. If the tree burns up in the forest fire it will release its carbon into the atmosphere instantly. The high rate of carbon storage can be maintained by transforming the trees into lumber. By storing the carbon in the form of lumber, the carbon released into the air can be offset by others means.

2.4 Hydrothermal Carbonization Process

There are many methods to produce advanced materials. One of them is hydrothermal processing. This technique enables the production of complex materials with interesting physicochemical properties. A wide range of materials such as metals, oxides, hydroxides, silicates, carbonates, phosphate and sulphates are being produces by this technique as nanostructure particles. (Guiotoku et al, 2011). Carbonization is one of the possible thermo chemical conversions of biomass into energy, where a solid residue known as charcoal is produced through a slow process of partial thermal decomposition of wood in the absence or controlled presence of oxygen. (Bridgwater, 2003). Same goes to Langner (2008), the HTC is an promising process to produce coal from biomass. Imitating the natural way of coalification in a chemical process, it has several advantages. One of them is the fact that no undesired byproducts produces. Particularly there will be no CO_2 as byproduct. This is a big difference to most of the other biomass energy processes. So by storing away the carbon for example as a newly-developed carbon-based insulating material, the process is able to reduce the CO_2 in the atmosphere. From the above statement it confidently prove that this process is more green and environmental friendly.

According to Yoshimura and Byrappa (2008), a hydrothermal process can be defined as any homogenous or heterogeneous chemical reaction in the present of solvent (whether aqueous or non-aqueous) above room temperature and at pressure greater than 1 atm in a closed system. Basically, the method consists of heating the biomass in the presence of a catalyst in a closed vessel under pressure, at temperature ranging from

180^{o}C to 300^{o}C, with reaction times between 1 and 48 hours. Thus, the hydrothermal carbonization allows the use of stored energy in biomass more efficiently. Theoretically, in anaerobic conversion, about 18% of energy is lost and 50% of carbon is released as carbon dioxide. In the HTC process, the carbon efficiency is very close to 100 which means the almost the carbon from biomass is converted into carbonized material, without generating CO and CO_2. (Titirici, 2007)

Some studies from Ramke *et al* (2009), hydrothermal carbonization (HTC) is a chemical process which emulates the natural coalification of biomass. First experiments were carried out by Bergius (1913), who described the hydrothermal conversion of cellulose into coal-like materials, and systematic investigations were performed in the nineteen-thirties. The process was rediscovered some years ago at the Max-Planck Institute of Colloids and Interfaces in Golm/Potsdam (MPI), where comprehensive state-of-the-art experiments helped to understand the process much more in detail. In co-operation with the MPI the University of Applied Sciences Ostwestfalen-Lippe started the first feasibility study on the HTC process using organic waste, funded by the DBU (Deutsche Bundesstiftung Umwelt), in 2007. Within the scope of this project more than 100 carbonizations were performed in a 25-litre pressure vessel. For hydrothermal carbonization to take place, plant-based products such as leaves, straw, grass, wood chippings or fir cones are placed in a pressure vessel together with water and a suitable catalyst. The reactor is then closed, and under air-exclusion is heated under pressure. The HTC process generally takes place at temperatures between 180°C and 220°C over a 4 to 12 hour period, after which, the mixture is cooled down and the vessel is opened: It now contains a black watery fluid comprised of finely dispersed spherical carbon